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Electronic properties of mixed transition metal clusters: Co clusters embedded in Ag

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We report on a systematic study of the electronic and magnetic properties of small Co clusters covered with Ag (Co_N Ag_M, N+M up to 297). The properties of these mixed transition metal clusters are related to the experimental arrangements observed in granular systems. For example, it has been reported that the GMR effect of these granular systems depends on their size, shape and magnetization. Up to now very few calculations have been performed to describe embedded clusters, while the experimental work has been growing steadily. It is therefore of interest to calculate the magnetization in order to explore the influence of cluster size and shape. We show that, for a given number of Co atoms, the total magnetic moment per Co depends on the size and shape of the Ag covering. We compare with 3D FLAPW calculations done for some particular structures.

Keywords: Mixed clusters; magnetism; GMR

Presentamos los resultados de un estudio sistemático de las propiedades electónicas y magnéticas de agregados pequeños de Co recubiertos con Ag ($Co_N Ag_M$, $N+M$ hasta 297). Las propiedades de estos agregados mixtos de metales de transición están vinculados con fenómenos físicos observados en sistemas granulares, como por ejemplo, el hecho de que el efecto GMR en estos sistemas depende del tamaño, forma y magnetización de los mismos. Hasta hoy se han realizado pocos cálculos para describir cúmulos revestidos. Mostramos en este trabajo que agregados, con un número dado de átomos de Co, muestran un momento magnético total que depende del tamaño y la geometría del recubrimiento, debido a que la plata puede presentar una polarización ferro o antiferro. Comparamos con cálculos FLAPW realizados para algunos casos particulares.

Descriptores: Cúmulos mezclados; magnetismo; GMR

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1. Introduction

The study of small metallic clusters has been the subject of wide investigation in recent years. This is due to the fact that clusters have electronic, optical, magnetic and structural properties different from those observed in the bulk. In particular, the magnetic properties of small transition metal clusters are technologically very attractive because of their magnetic recording applications and also due to their chemical reactivity in connection with catalytic processes.

On the side of the homonuclear clusters, it has become possible to study free metallic ones by examining the Stern-Gerlach deflection pattern of individual mass-selected clusters, and the magnetic moments can be measured as a function of size. For example, Fe, Co and Ni clusters show large magnetic moments per atom which decrease slowly and non-monotonously to the bulk values with increasing size. Actually, the magnetic moments reach the bulk values for clusters larger than 700 atoms [1–3].

Granular magnetic solids, consisting of single-domain ferromagnetic particles embedded in an inmiscible medium, have also been studied in recent years because of their potential use in magnetic recording, optical devices and sensors. For example, giant magnetoresistance (GMR) has been recently observed in granular films of magnetic clusters embedded in a non magnetic metal [4, 5]. The magnetoresistance is directly related to the macroscopic magnetization, and therefore also to the grain size distribution and the intergranular magnetic interactions [6].

Although there has been a large computational effort in studying homonuclear clusters and also supported or adsorbed clusters, specially dimers [7], only a few calculations have been done on mixed clusters. *Ab initio* calculations by Chuanyun *et al.* [8] for Co clusters embedded in Cu, and also the tight-binding calculations by Vega *et al.* [9] for Fe clusters embedded in Cr, are some examples.

In this contribution we show the results of calculations for Co clusters coated with Cu and Ag ($Co_N X_M$, X = Cu, Ag, $N+M$ up to 297) as increasing parts of a fcc lattice. We focus mainly on the Co-Ag systems, and the calculations for Co-Cu clusters are done in order to compare with *ab initio* results.

The purpose of this systematic study is to analyze the behavior of the magnetic moment of these mixed clusters as a function of shape, size and composition, as the magnetic properties of mixed transition metal (TM) clusters are not necessarily given by the average behavior of the corresponding bulks [10]. We show that the polarization of the noble metal, which coats the Co clusters, is very sensitive to the symmetry of the system, for example Ag can develop an antiferro- or ferromagnetic alignment with Co by changing the atomic arrangement of the noble metal. This can lead to variations in the magnetic moment of the whole sample, while keeping the magnetization of the Co atoms quite unaltered. Most of our calculations are performed with a parametrized hamiltonian [11] but we also find this effect when doing LAPW *ab initio* calculations for some selected systems using the WIEN97 code [12].

2. Method for cluster calculations

As in previous works, a tight-binding Hamiltonian with *spd* orbitals and parameters taken from the corresponding bulk materials is used for the cluster calculations. Magnetism is obtained from a Hubbard-like term solved in the unrestricted Hartree-Fock approximation and only nearest neighbor two center parameters are considered. All many-body contributions appear in the diagonal term, $\epsilon_{im\sigma}$, and are given by

$$\epsilon_{im\sigma} = \epsilon^0_{im} + \sum_{m'} U_{imm'} \Delta\eta_{im'} - \sigma \sum_{m'} \frac{J_{imm'}}{2} \mu_{im'} + \Delta\epsilon_i^{\mathrm{MAD}} \qquad (1)$$

where $\Delta\eta_{im'}$ is the electronic occupation difference per orbital in the i-th atom of the cluster with respect to the bulk paramagnetic values, $\mu_{im'}$ is the magnetization per orbital and $\Delta\epsilon_i^{\mathrm{MAD}}$ is the Madelung term.

The single-site energies ϵ^0_{im} and the hopping elements of the Hamiltonian are taken to be equal to the bulk values obtained from Andersen's canonical LMTO-ASA paramagnetic bands [13]. The hopping parameters are assumed to be always spin independent and the heteronuclear ones at the Co-X (X = Cu, Ag) interfaces are averaged as in Ref. 14, within an approximation similar to the one already used by Victora and Falicov for Co overlayers on Cu(111). [15]

$U_{imm'}$ are the screened intrasite Coulomb integrals in the solid. The values U_{idd} are obtained using our bulk occupations following Ref. 16 and the U_{iss}/U_{idd} relations are taken from atomic tables. $J_{imm'}$ are the intrasite exchange integrals and are assumed to be zero except for d orbitals. J_{idd} is fitted to obtain experimental bulk magnetizations.

The Madelung term, $\Delta\epsilon_i^{\mathrm{MAD}}$, must be added because of the presence of large charge transfers among shells within the clusters. It consists of the sum of electrostatic potentials over all cluster sites:

$$\Delta\epsilon_i^{\mathrm{MAD}} = \sum_{l \neq i} V_{il} \qquad (2)$$

where V_{il} contains the interatomic electrostatic interactions between atoms on sites $\mathbf{R}_i$ and $\mathbf{R}_l$. For a bulk parametrization an expression commonly used in alloys and multilayers as in Ref. 17 is appropriate,

$$V_{il} = \frac{U}{1 + U|\mathbf{R_i} - \mathbf{R_l}|} \Delta\eta_l, \qquad (3)$$

where $\Delta\eta_l$ is the total electronic occupation difference with respect to the paramagnetic bulk values on the l-th atom of the cluster. Taking into account that in late transition metals there are more d than sp electrons, we have taken for U the average of the Co and noble metal values for d orbitals.

Extra orbitals s' outside the clusters are added to account for electron spill over at the surfaces and we parametrize them in order to get adequate d orbital occupations. The selection of the s'-orbital site energy is related to the average coordination of the surface atoms. The number of s' orbitals added is such that each cluster atom keeps its bulk coordination. [11]

We select for our calculations those isomers of high symmetry (O_h or D_{4h}) always part of fcc lattices. We consider the fcc structure as the most probable one for the clusters, as both components are fcc in the bulk phase and also recent experiments show that Co clusters grow in the fcc structure for small sizes. [18] By using techniques of group theory and therefore by convenient symmetrization of the basis functions, we can calculate up to 297 atom clusters (14 shells in a fcc structure).

3. Results

3.1. Co-Cu clusters

Tight-binding calculations for Co-Cu clusters are compared with *ab initio* results by Chuanyun *et al.* [8]. The total magnetic moment for $Co_N Cu_M$, with $13 \leq N + M \leq 135$, is shown in Table I. The comparison with the available *ab initio* results is excellent, the total magnetic moments are equal, even if the distribution within the shells differs somewhat.

3.2. Co-Ag clusters

Co and Ag have very different lattice constants and therefore the interatomic distances in the clusters are not known. Thus, we use the FLAPW *ab initio* WIEN97 code for help [12].

We calculate, for example, the $CoAg_3$ ordered alloy in the $L1_2$ structure, in which the Co atoms have 12 Ag nearest neighbors and optimize the cell size. The cell constant obtained is equal to 7.35 au, which is intermediate between Co (6.7 au) and Ag (7.6 au) bulk values. In all cases the calculations are converged with 64 k-points in the irreducible zone, RKM = 8 and the Ceperley-Alder exchange-correlation potential is used. The magnetic moments obtained are: for Co 1.45 μ_B, for Ag $-.02\,\mu_B$, and the polarization of the intersti-

TABLE I. Total magnetic moment per cluster in the case of Co embedded in Cu. N_{Co} is the number of Co atoms and N_{tot} is the total number of Co and Cu atoms. Also shown are the magnetic moments corresponding to the bare Co clusters ($N_{Co} = N_{tot}$). The *ab initio* results by Chuanyun *et al.* [8] are given in brackets and bold characters. All the magnetic moments are in μ_B.

N_{tot} / N_{Co}	13	19	43	55	79	87	135
13	27	25	23**[23]**	27	21	26	23
19		39	35**[35]**	39	33	31	35
43			84	81**[81]**	77	75	77
55				102	95	87	89
79					151	135	137
87						164	151
135							247

tial region is $-.07\,\mu_B$. The magnetic moment of Co (μ_{Co}) is lower than the corresponding bulk value and the Ag's are in this case antiferromagnetically aligned (AF).

We also analyze a Co1/Ag1 superlattice grown along the (001) direction. The inplane distance taken is the Ag bulk one, as expected for an epitaxial growth on a Ag substrate. By optimizing the Ag-Co distance in the (001) direction, we obtain an interplane separation of 3.15 au. The Co-Ag optimized distance in the $CoAg_3$ alloy is 5.20 au, while in the superlattice it is 4.94 au. The previous results justify considering, in our Co-Ag cluster calculations, for the Co-Co and Ag-Ag distances the corresponding bulk parameters , and for the Co-Ag one the average one.

As in the case of the Co-Cu systems, we calculate for Co_NAg_M clusters with $N + M$ going from 13 to 297, and consider always closed atomic shells as part of a fcc structure. In Table II we show the total magnetic moments of the clusters (Co atoms plus Ag atoms) and in parenthesis the magnetic moment of just the Co cores. There are cases where the Ag net polarization can be ferromagnetic (F) with respect to the Co core but for most of the considered cases the Ag net polarization is AF. The total magnetic moment of the clusters is almost always smaller than the one corresponding to the bare Co clusters, while the average magnetization of the Co core is larger than the Co bulk value.

In Table III we show the magnetic moment per atom, orbital and shell for two Co-Ag clusters with the same number of Co atoms ($Co_{13}Ag_{198}$ and $Co_{13}Ag_{284}$). The total average magnetic moment per Co atom (total magnetic moment of the cluster over the number of Co atoms) of these clusters is 1.61 μ_B and 1.23 μ_B, respectively. This large decrease in the total magnetic moment is due to the fact that in the second cluster there are many more AF Ag atoms surrounding the Co core than in the first one. Even if each Ag atom contributes with a very small polarization, in both cases the polarization is mainly AF and in the second case we have 96 Ag's more than in the first one. In Table III it is seen that the d-polarization of the Ag atoms dies down very fast, while the sp-one can be still rather large in the outermost shell of a 14-layer cluster. It is interesting to note that the total magnetic moment of the Co core is nearly the same in both cases discussed (see Table II). This explains the remarkable fact that for a fixed number of Co atoms, there is an astonishing broad range of cluster magnetizations that can be attained by just changing the Ag covering, as can be observed in Table II.

TABLE II. Total magnetic moment per cluster in the case of Co embedded in Ag. N_{Co} is the number of Co atoms and N_{tot} is the total number of Co atoms and Ag atoms. The magnetic moments of the Co core are given in parenthesis. All the magnetic moments are given in μ_B.

N_{tot} / N_{Co}	13	19	43	55	79	87	135	141	177	201	297
13	27	27(27.2)	25(25.6)	27(25.9)	21(23.9)	27(26.6)	23(23.4)	23(23.6)	23(23.2)	21(23.3)	16(22.5)
19		39	36(37.0)	39(37.9)	33(34.4)	34(34.9)	35(34.5)	35(35.6)	35(33.8)	31(32.7)	21(32.0)
43			84	81(83.6)	81(82.2)	85(84.3)	77(77.7)	75(77.2)	71(74.8)	76(77.9)	63(72.0)
55				102	97(100.7)	87(93.0)	95(96.3)	99(99.5)	95(95.9)	97(96.7)	83(91.4)
79					151	135(140.2)	137(140.1)	141(142.5)	137(138.2)	139(139.2)	132(145.0)
87						164	153(156.7)	157(159.4)	145(150.5)	154(155.0)	145(150.6)
135							247	241(246.2)	237(242.4)	223(230.9)	229(232.9)
141								253	249(253.8)	235(242.5)	243(244.9)
177									317	307(316.2)	307(312.0)
201										351	355(359.5)
297											497

TABLE III. Magnetic moments per atom and per orbital, in μ_B. The first column indicates shell number in increasing order.

$Co_{13}Ag_{198}$			
shell	μ_d	μ_{sp}	$\mu_{\rm tot}$
1(Co)	1.58	−0.12	1.46
2(Co)	1.87	−0.05	1.82
3(Ag)	0.03	−0.08	−0.05
4(Ag)	0.02	−0.04	−0.02
5(Ag)	0.01	−0.03	−0.02
6(Ag)	0.00	−0.02	−0.02
7(Ag)	0.00	−0.01	−0.01
8(Ag)	0.00	0.00	−0.00
9(Ag)	0.00	−0.02	−0.02
10(Ag)	0.00	−0.01	−0.01
11(Ag)	0.00	0.00	−0.00
$\mu_{s',tot} = -0.13$			
$Co_{13}Ag_{284}$			
shell	μ_d	μ_{sp}	$\mu_{\rm tot}$
1(Co)	1.94	−0.10	1.84
2(Co)	1.77	−0.05	1.72
3(Ag)	0.04	−0.08	−0.04
4(Ag)	0.01	−0.05	−0.04
5(Ag)	0.01	−0.04	−0.03
6(Ag)	−0.01	−0.02	−0.03
7(Ag)	0.00	−0.01	−0.01
8(Ag)	−0.01	−0.01	−0.02
9(Ag)	0.00	−0.01	−0.01
10(Ag)	0.00	−0.01	−0.01
11(Ag)	0.00	−0.02	−0.02
12(Ag)	0.00	−0.01	−0.01
13(Ag)	0.00	−0.02	−0.02
14(Ag)	0.00	−0.02	−0.02
15(Ag)	0.00	−0.02	−0.02
$\mu_{s',\rm tot} = -0.83$			

In Figs. 1 and 2 we plot the magnetic moment of the Co core and the total magnetic moment $(N + M)$, always per Co atom, for two of the examples of Table II, namely, $N_{\rm Co} = 13$, and 43 as a function of $N + M$. We join the data with lines just as a guide to the eye, but one has to keep in mind that we have calculated for only three clusters between $N_{\rm tot} = 150$ and 300. It is evident that the total magnetic moment not only depends on the number of Co atoms of the core but also on the number and shape of the surrounding Ag capping. The Ag net polarization oscillates, but the overall tendency for increasing number of Ag shells seems to be towards an AF net polarization. In this sense it is interesting to point out that even for the largest cluster sizes considered, the outer Ag shells and the spilled over electrons still acquire an AF polarization.

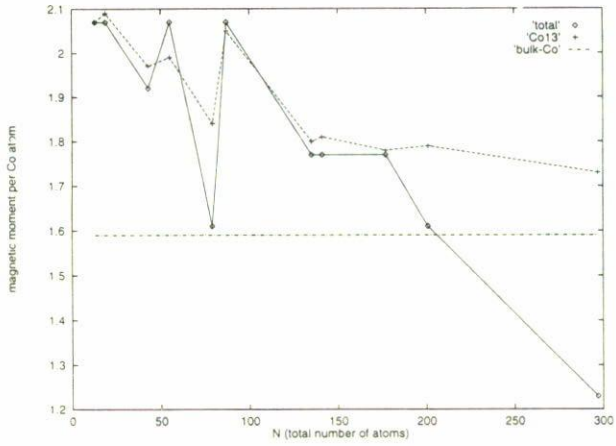

FIGURE 1. Magnetic moment per Co atom as function of increasing number of Ag atoms for $Co_{13}Ag_M$ cluster. ($\diamond$) corresponds to the total magnetic moment, (+) to the magnetic moment of the Co_{13} core.

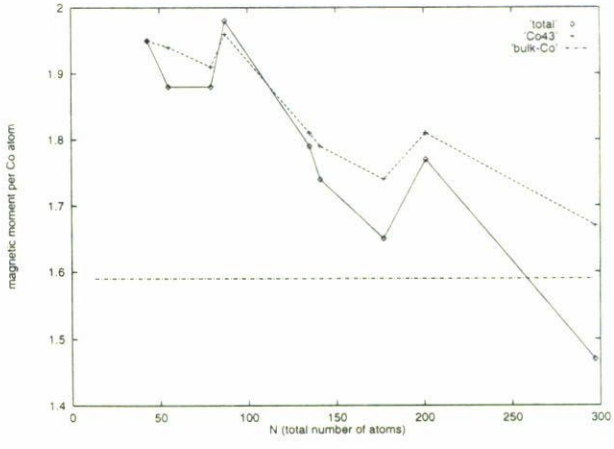

FIGURE 2. *Idem* Fig. 1 but for $Co_{43}Ag_M$.

Relative maxima in the magnetization per atom occur for some sizes. They are related to an increased ferro alignment of the Ag atoms. For instance, in Co_{13} for $N + M = 55$ and 87, and in Co_{43} for $N + M = 87$, the Ag net polarization is slightly F with respect to the Co central cluster. The structure of the clusters, for which the Ag atoms have a net F polarization, shows spikes in the outer Ag shell.

In order to check that the total magnetization depends on the number and distribution of the noble metal atoms surrounding Co we have calculated two enlightening examples using the WIEN97 package [12]. In the first case we consider a fcc trilayer grown in the (001) direction, the central layer is a 2D ordered AgCo (50% each) alloy, the outer layers are pure Ag. This means that we consider three (001) planes of the $CoAg_3$ previously optimized alloy. The systems being 3D periodic, we take an interslab distance three times the slab width so that the surfaces do not interact. In this case each Co atom is surrounded by 12 Ag nearest neighbors and 4 Co next nearest neighbors. The slab surfaces are perfect planes.

For the second example we consider the same supercell, but we add one Ag atomic plane on each side of the slab with 50% of the atoms missing, showing a (2×2) surface structure. In this last case, each Co atom has the same first and second nearest neighbor structure as before, and the surface presents spikes.

We use 42 k-points in the irreducible zone and RKM $= 8$, in both examples. The magnetic moments of the cells are 1.23 μ_B and 1.53 μ_B respectively. Changing the Ag surface from a perfect plane to a less flat one switches the polarization of the Ag atoms from AF to F and the cell magnetization increases 0.3 μ_b, while the change in the local magnetization of the Co atoms is of only 0.1 μ_B. This effect is similar to the one observed in Figs. 1 and 2, for those clusters for which there are relative magnetization maxima. For $N = 55$ and $N = 87$ the outer Ag shell is not flat but presents spikes and the net Ag polarization is F, while for smoother surfaces the net Ag polarization is AF. This explains the relative maxima at $N = 55$ and $N = 87$.

4. Discussion and conclusions

From the results of our calculations it is seen that Ag becomes polarized even at large distances from the Co cores. The Ag net polarization can be F or AF, due to the sp orbitals of Ag, while the Ag d polarization dies down at nearest neighbor distances. This long-range effect reflects itself in the broad range of magnetizations that a given Co core can display depending on Ag covering. The total magnetizations can be much less than the contribution coming just from Co. This effect is also expected if instead of Ag a Cu covering is present.

Recently, Eastham *et al.* have measured a quenching of ferromagnetism in cobalt clusters embedded in copper by using magnetic X-ray circular dichroism [19]. This behavior can be explained by our calculations. Magnetic interaction through a noble metal spacer were also observed in two other types of experiments. The first one, the oscillatory exchange coupling is already well known [20]. A second, the exchange bias was recently reported. [21] In both experiments two magnetic layers interact when separated by up to 50–100 Å of Cu.

When the covering is thin, symmetry effects show up and there is a switch from AF to F polarization of the Ag atoms depending on the presence of spikes on the Ag surface. This was also observed in 3D LAPW *ab initio* calculations. Calculations for intermediate and larger cluster sizes are in progress.

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1. S.E. Apsel, J.W. Emmert, J. Deng, and L.A. Bloomfield, *Phys. Rev. Lett.* **76** (1996) 1441.
2. I.M.L. Billas, A. Châtelain, and W.A. de Heer, *Science* **265** (1994) 1682.
3. I.M.L. Billas, J.A. Becker, A. Chatelain, and N.A. de Heer, *Phys. Rev. Lett.* **71** (1993) 4067.
4. F. Parent *et al.*, *Phys. Rev.* **B55** (1997) 3683.
5. A.E. Berkowitz *et al.*, *Phys. Rev. Lett.* **68**, (1992) 3745; J.Q. Xiao, J. Samuel-Jiang, and C.L. Chien, *ibid.* **68** (1992) 3749.
6. E.F. Ferrari, F.C.S da Silva, and M. Knobel, *Phys. Rev. B* **56** (1997) 6086.
7. H. Dreysse and C. Demangeat, *Surf. Sci. Reports* **28** (1997) 65.
8. X. Chuanyun, Y. Jinlong, D. Kaiming, and W. Kelin, *Phys. Rev. B* **55** (1997) 3677.
9. A. Vega, L.C. Balbas, J. Dorantes-Davila, and G.M. Pastor, *Phys. Rev.* **B50** (1994) 3889.
10. X.G. Li, A. Chiba, and S. Takahashi, *J. Magn. Magn. Mater.* **170** (1997) 339.
11. J. Guevara, F. Parisi, A.M. Llois, and M. Weissmann, *Phys. Rev. B* **55** (1997) 15289; *ibib Computational Materials Science*, (in press).
12. P. Blaha, K. Schwartz, and J. Luitz, **WIEN97**, Vienna University of thechnology 1997. [Improved and update Unix version of the original copyrighted WIEN-code, which was published by P. Blaha, K. Schwartz, P. Sorantin, and S.B. Trickey, *in Comput. Phys. Commun.* **59** (1990) 399].
13. O.K. Andersen and O. Jepsen, *Phys. Rev. Lett.* **53** (1984) 2471; O.K. Andersen, O. Jepsen, and D. Gloetzel, in *Highlights of Condensed Matter Theory*, edited by F. Bassani, F. Fumi, and M. Tosi, (North Holland, Amsterdam, 1985)
14. H. Shiba, *Prog. Theor. Phys.* **46** (1971) 77.
15. R.H. Victora and L.M. Falicov, *Phys. Rev. B* **28** (1983) 5232.
16. T. Bandyopadhyay and D.D. Sarma, *Phys. Rev. B* **39** (1989) 3517.
17. G. Fabricius, A.M. LLois, M. Weissmann, and M.A. Khan, *Phys. Rev. B* **49** 2121 (1994); G. Fabricius, A.M. Llois, and M. Weissmann, *ibid.* **44** (1991) 6870.
18. O. Kitakami *et al.*, *Phys. Rev. B* **56** (1997) 13849.
19. D.A. Eastham *et al.*, *J. Phys.: Condens. Matter* **9** (1997) L497.
20. J. Unguris, R.J. Celotta, and D.T. Pierce, *Phys. Rev. Lett.* **67** (1991) 140.
21. N.J. Goekemeijer, T. Ambrose, and C.L. Chien, *Phys. Rev. Lett.* **79** (1997) 4270.